

Thin Coatings of Polymeric Carbon and Carbon Nanotubes for Corrosion Protection

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2009 US Army Corrosion Summit

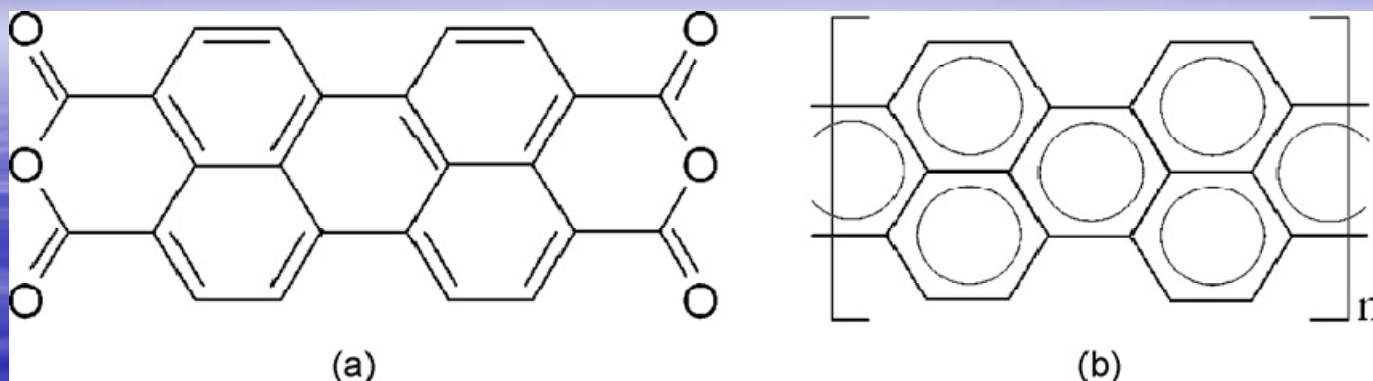


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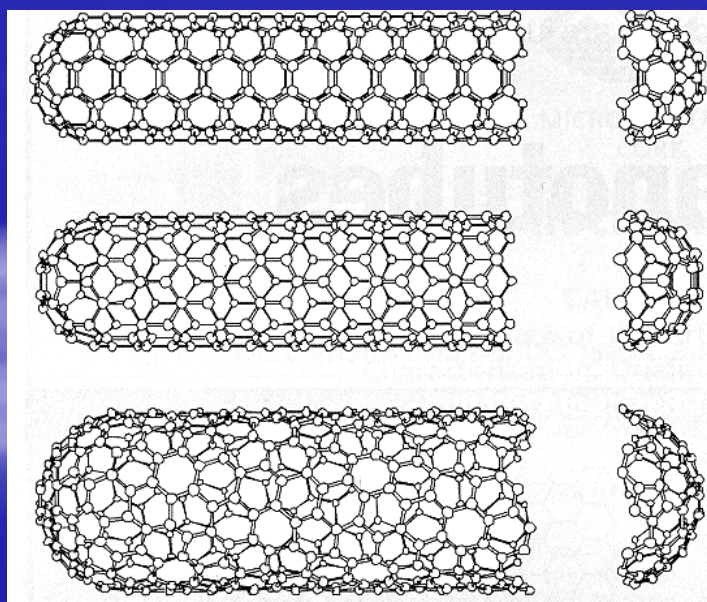
Outline of talk

- Introduction – new barrier materials and concepts for corrosion protection
 - Conjugated/conducting polymers
 - Smart-active corrosion protection with carbon nanotube *p-n* junctions
 - Potential corrosion protection in iron-carbon nanotube composites
- Polyperinaphthalene (PPN) results
- Carbon Nanotube approaches and results
- Thermochromic conjugated polymer concepts
- Summary

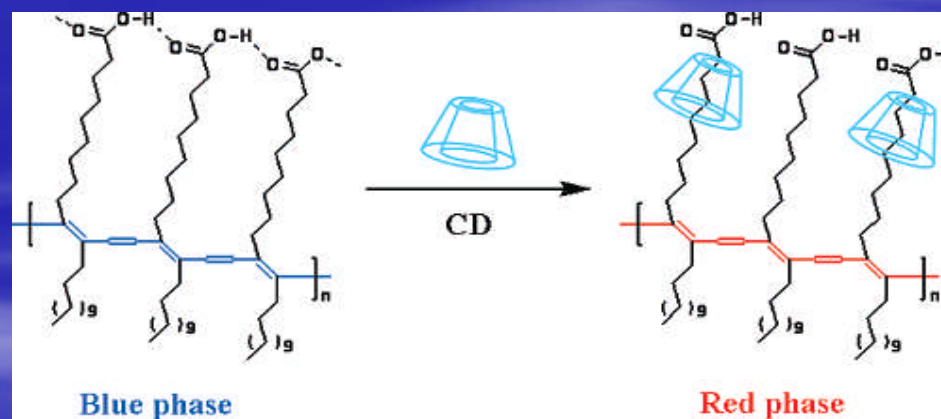
Chemical Structures of Coating Materials



Polyperinaphthalene (PPN)

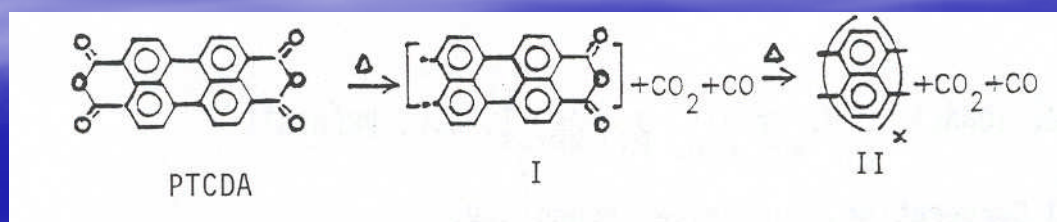
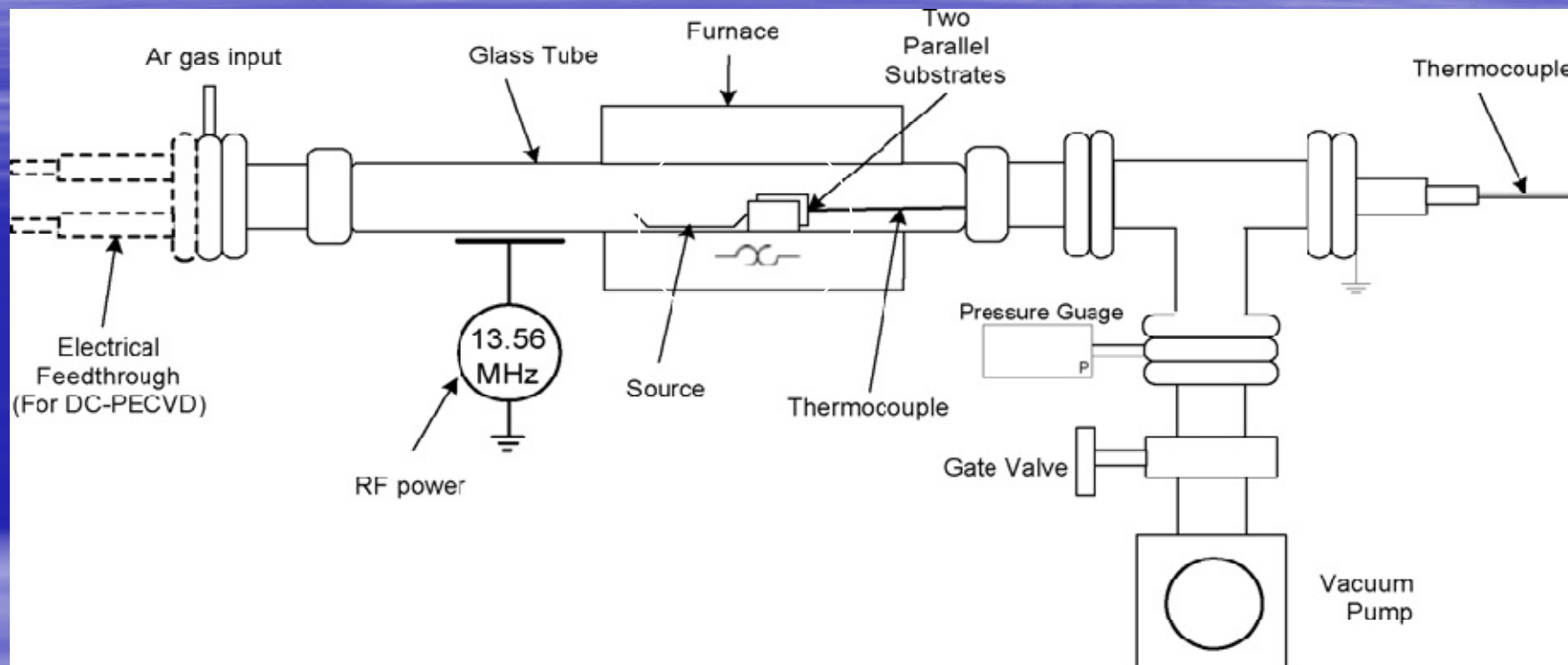


Single wall carbon nanotubes



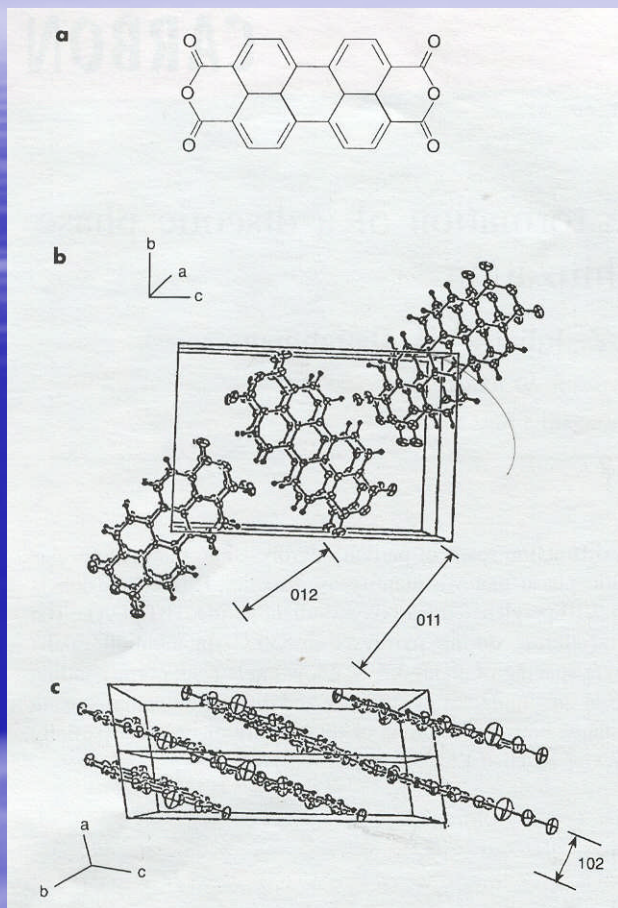
Polydiacetylene: $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-\text{COOH}$

Apparatus for Plasma-CVD Synthesis and Deposition of PPN

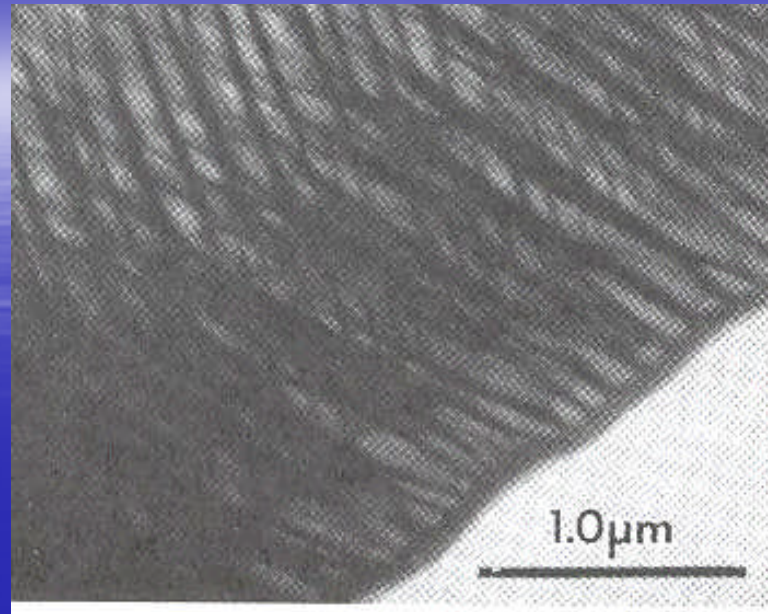


C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals* 158, 425 (2008)

Transition from PTCDA precursor to PPN

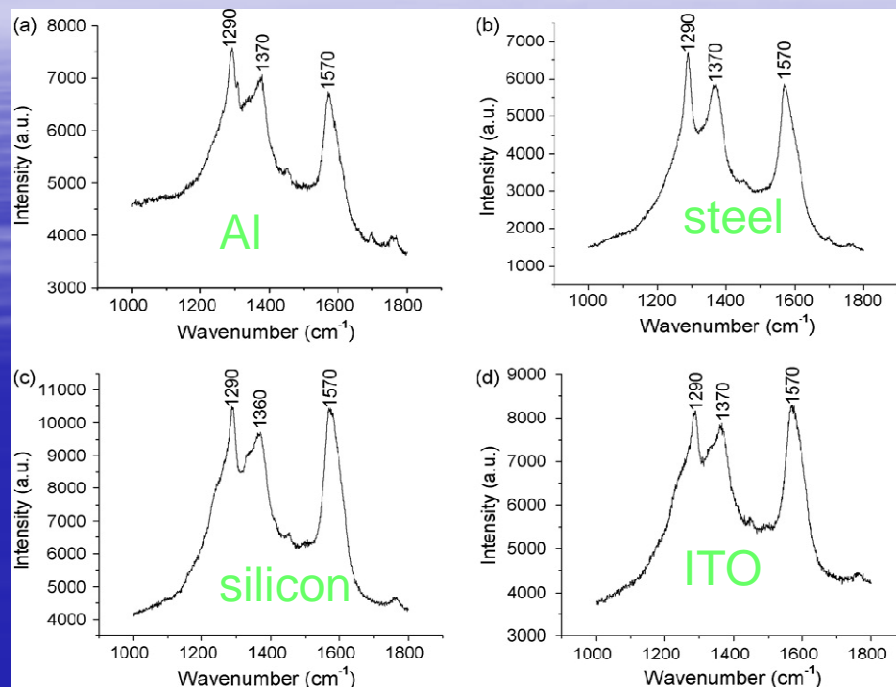


Crystal structure of
PTCDA precursor

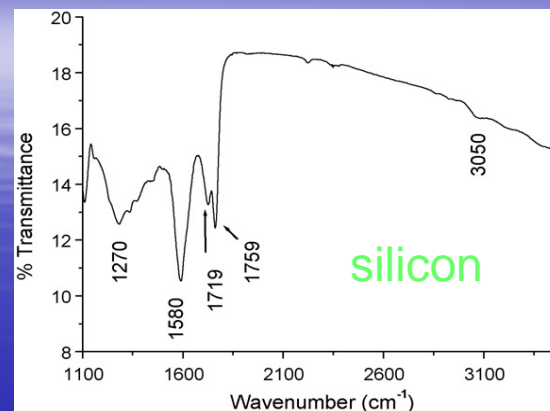


TEM images of PPN

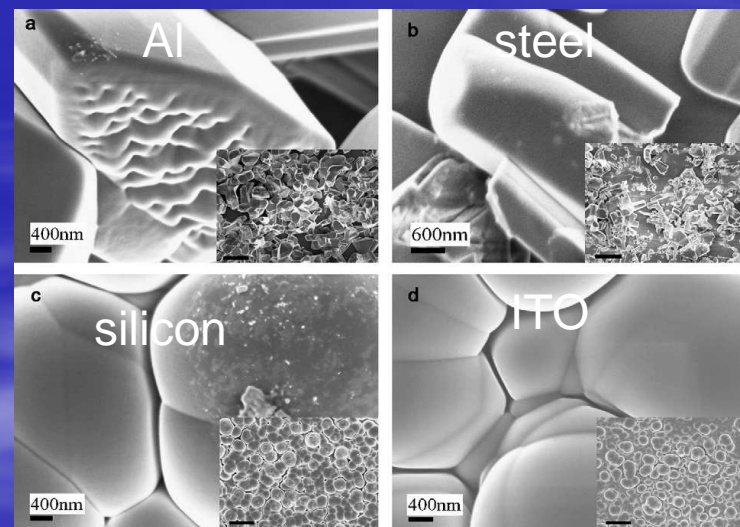
PPN Coating Characterization



Raman



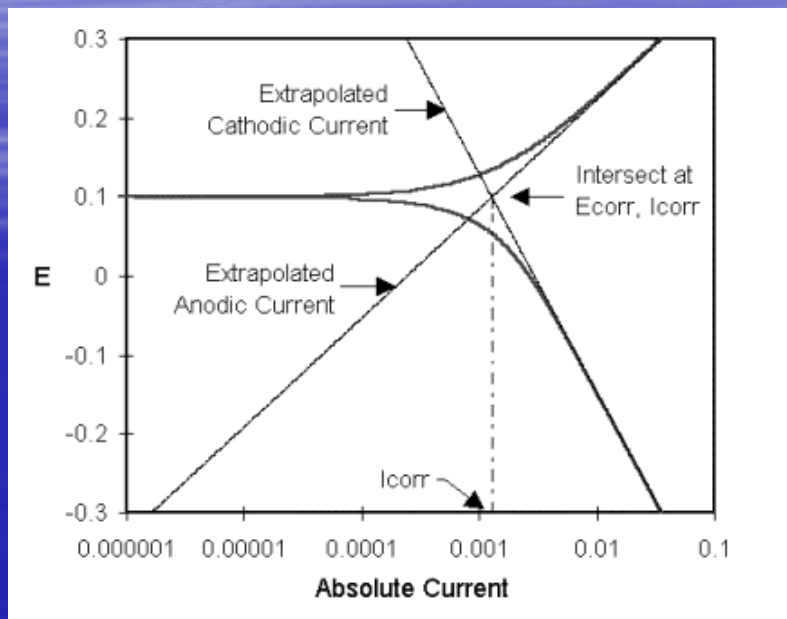
FTIR



SEM on different substrates

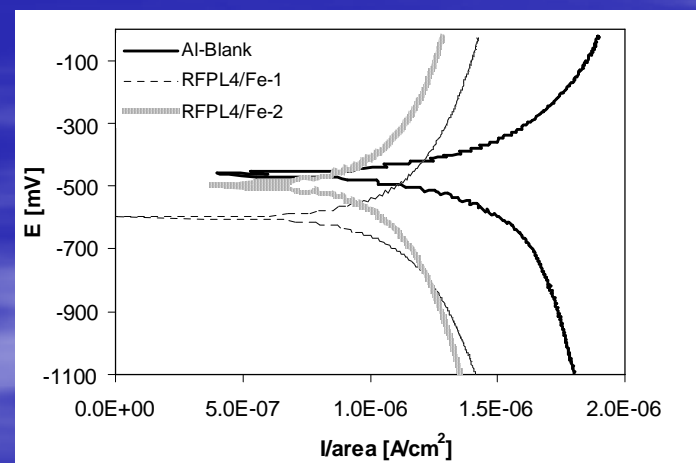
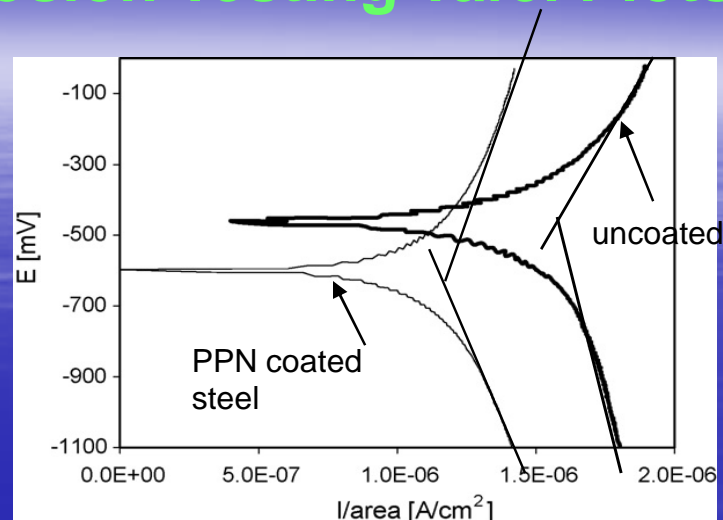
C. Yu, S. C. Wang, M. Sosnowski, and Z. Iqbal, *Synthetic Metals* 158, 425 (2008)

Potentiodynamic Corrosion Testing Tafel Plots



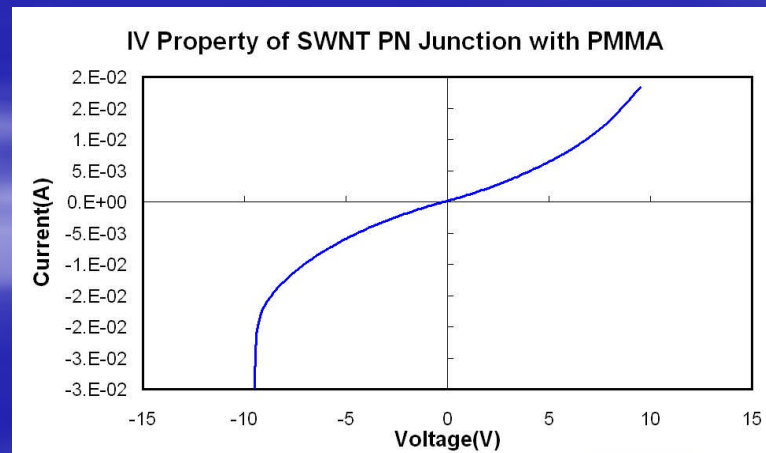
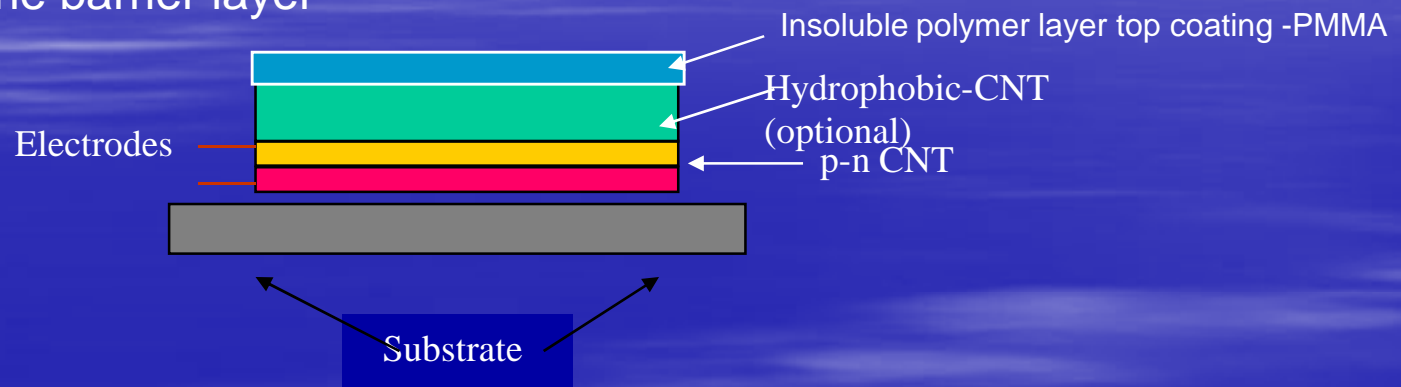
Applications:

- Corrosion protection for inaccessible device components
- Corrosion protection for fuel cell current collecting bipolar flow-field plates ["Corrosion Resistant Coated Fuel Cell Plate with Graphite Protective Barrier and Method of Making the Same", Z. Iqbal, T. Rehg, J. Guiheen and D. Narasimhan – US Patent 6,864,007 (2005) Honeywell-GE Power Systems].



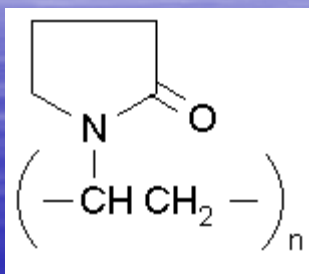
Multilayer Smart Carbon Nanotube Coating

- Paints of 3 types of carbon nanotubes prepared as paints or inks in polymers
- p-n doped layer functions as a transistor to monitor the health of the coating
- Top layer functionalized with hydrophobic (e.g. fluorine-containing) groups functions as the barrier layer



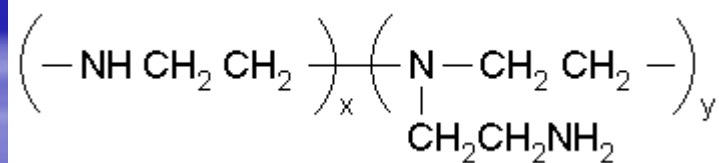
Carbon Nanotube Functionalization/Doping

A) *p*-Doping



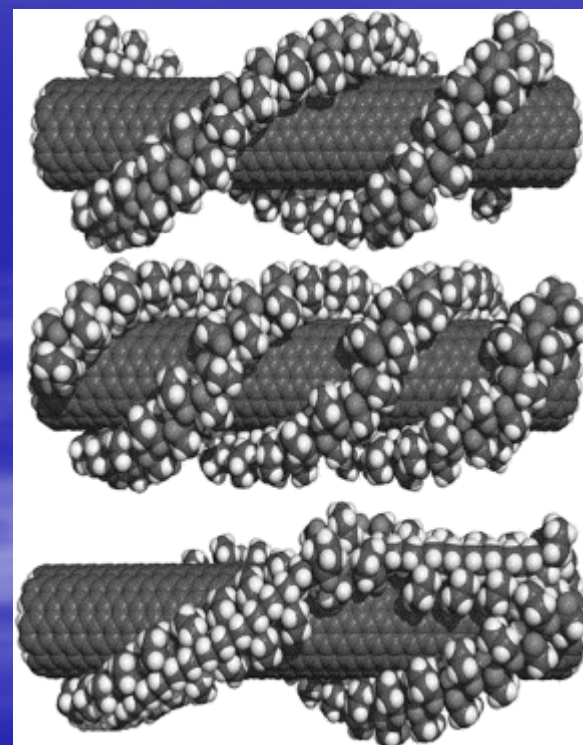
Polyvinylpyrrolidone (PVP)

B) *n*-Doping

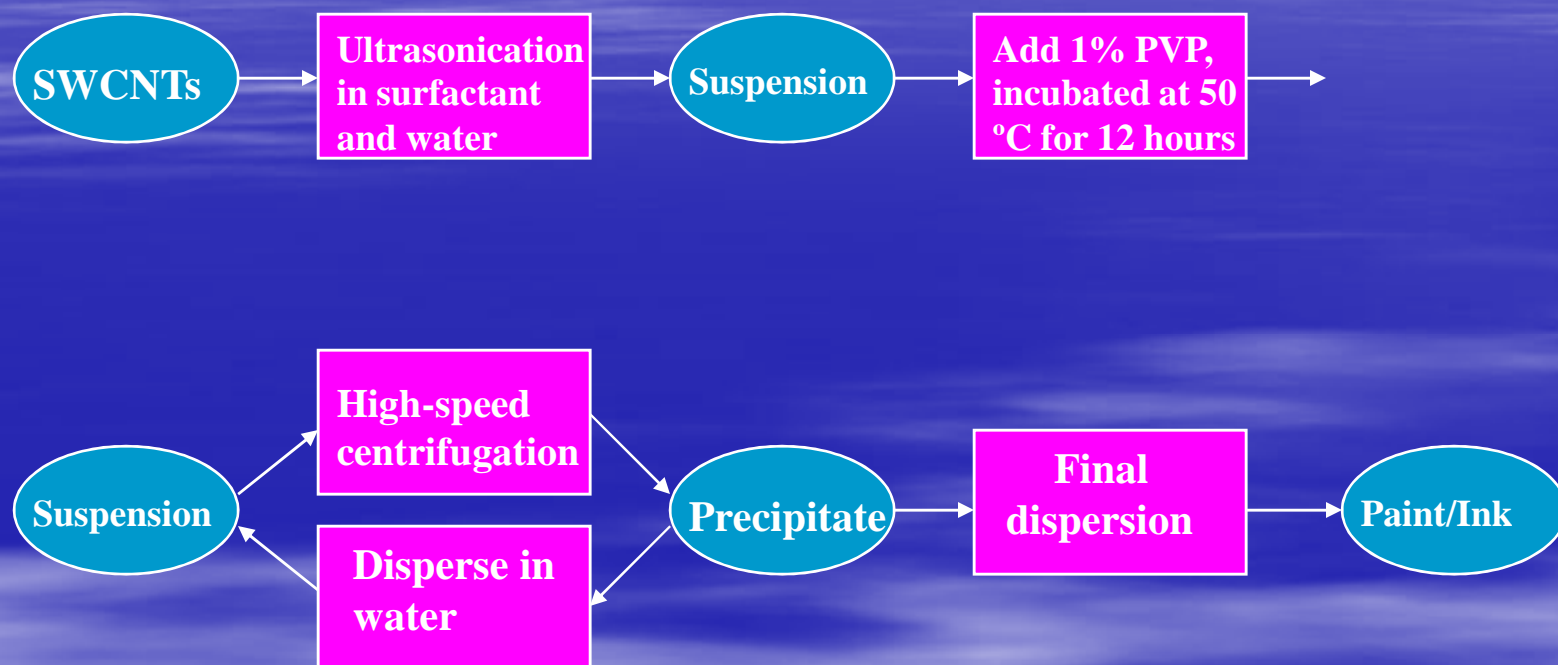


**Polyethyleneimine
(PEI)**

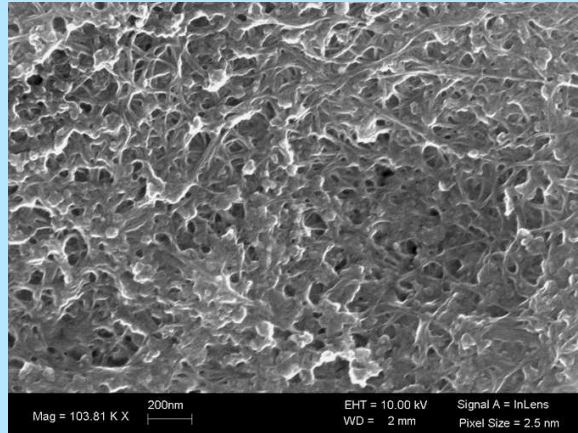
C) Polymer Wrapping Model



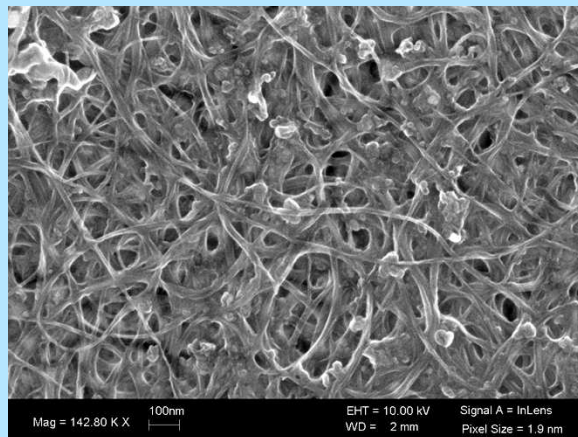
SWCNT Paint/Ink for Coatings



Multilayer Smart Carbon Nanotube Coating

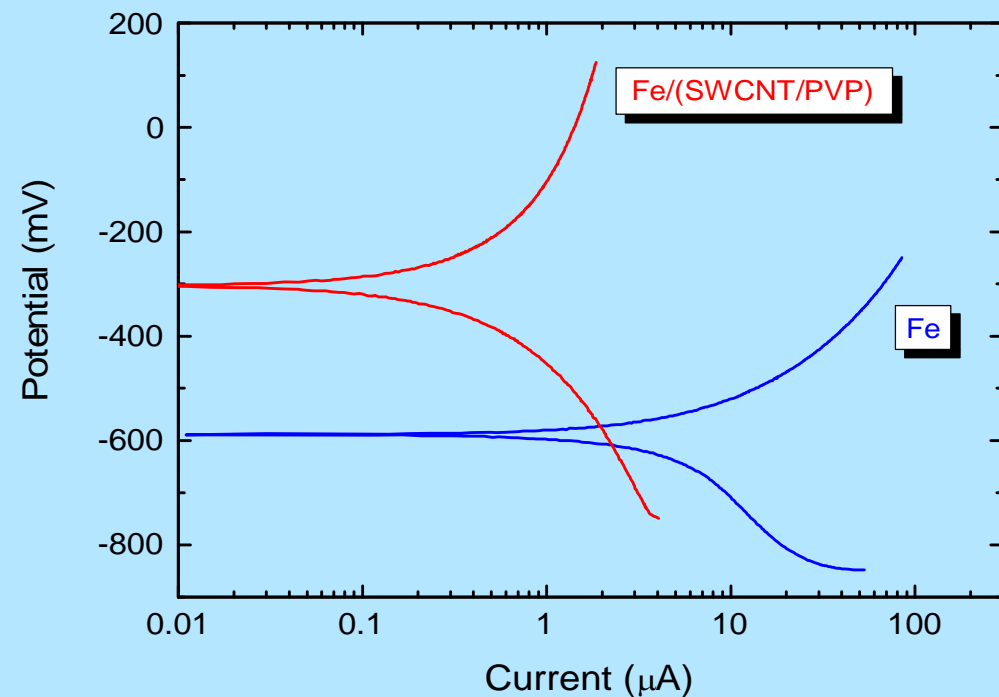


p-doped SWCNTs PVP



n-doped SWCNTs PEI

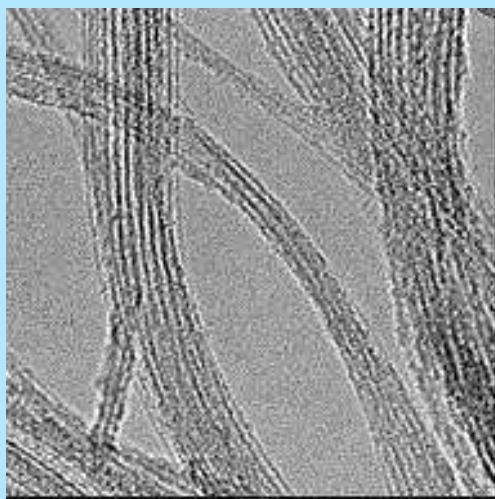
Tafel Plots of Coated and Uncoated Iron



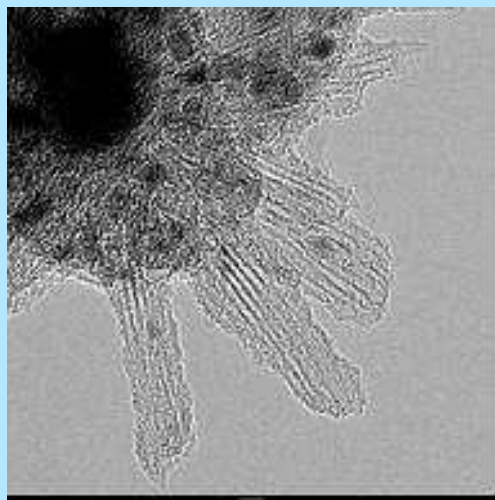
Corrosion current decreases with nanotube coating—thus improved corrosion protection

Multilayer Smart Carbon Nanotube Coating

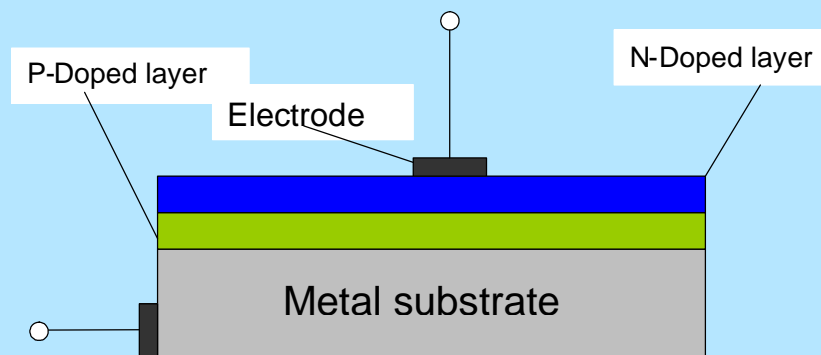
TEMs



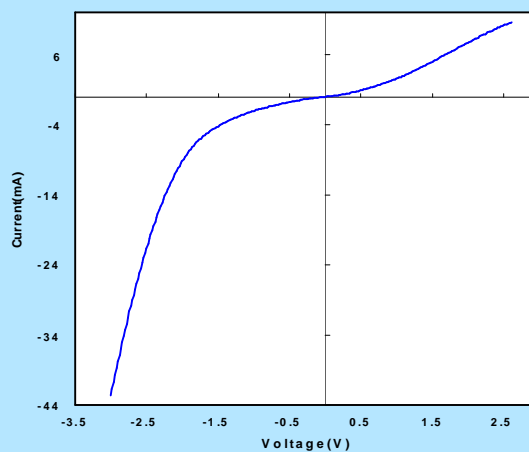
As-prepared SWCNTs



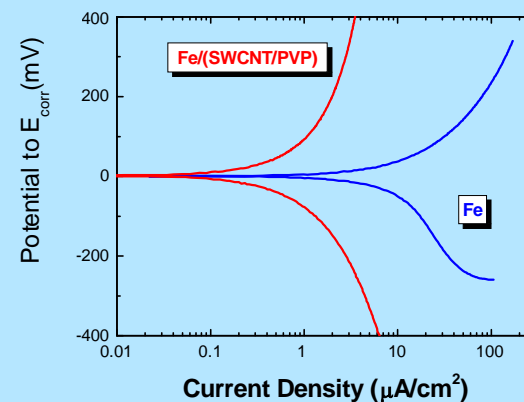
n-doped SWCNTs PEI



IV Property of Reflux PEI-P-T_2

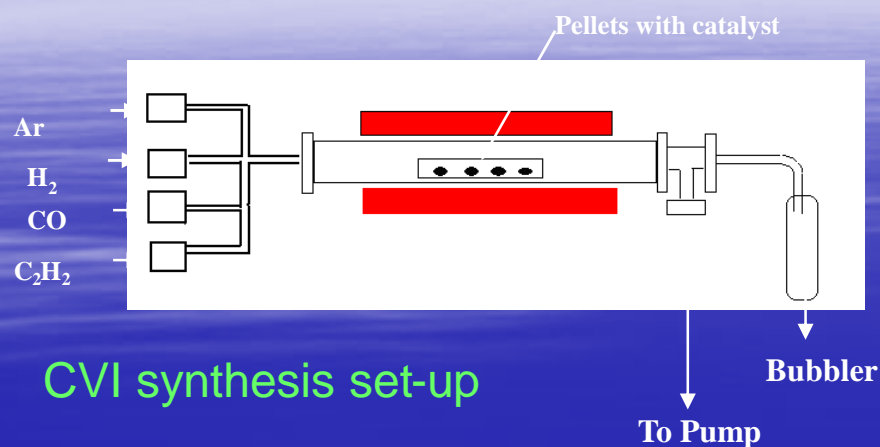
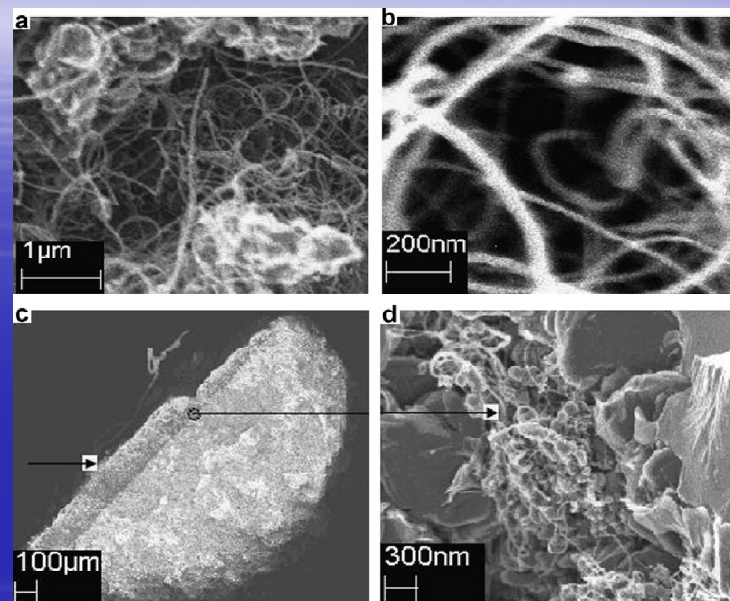


Tafel Plots of Coated and Uncoated Iron



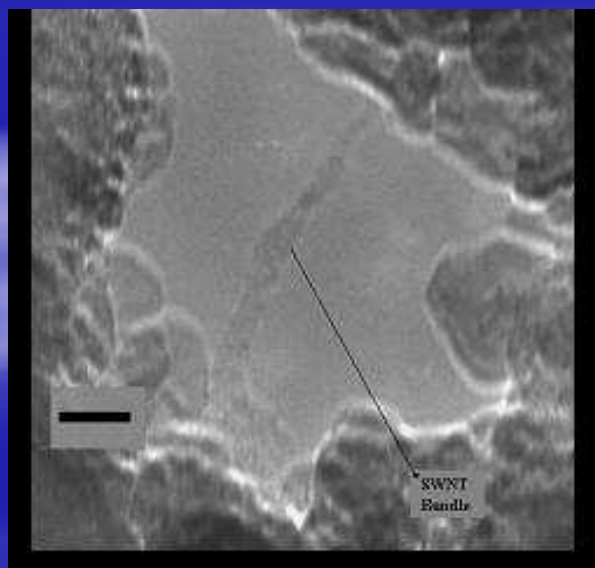
Potentially corrosion-resistant high strength bulk iron-carbon nanotube composites

SEM

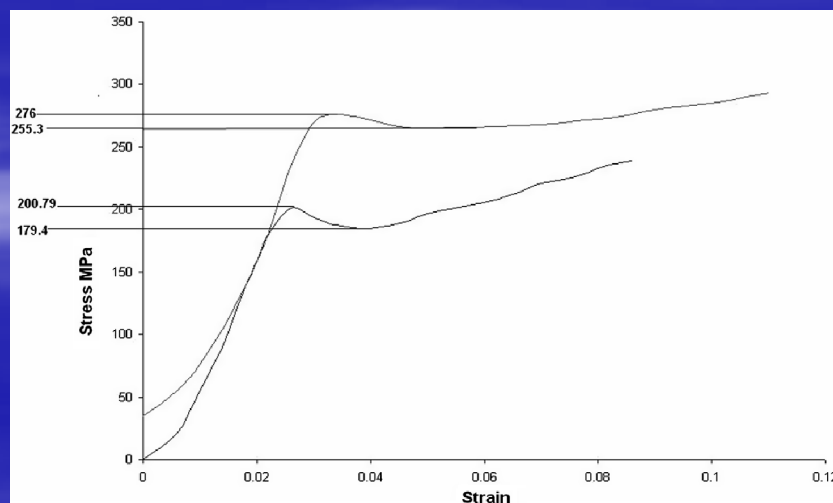


CVI synthesis set-up

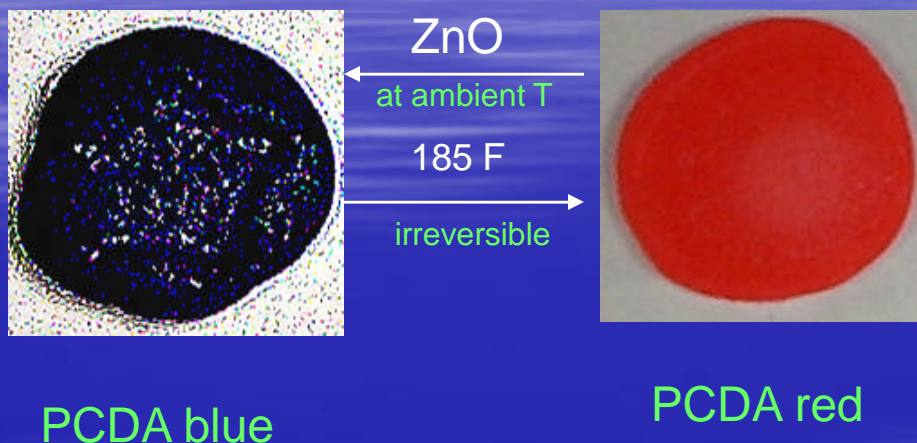
TEM



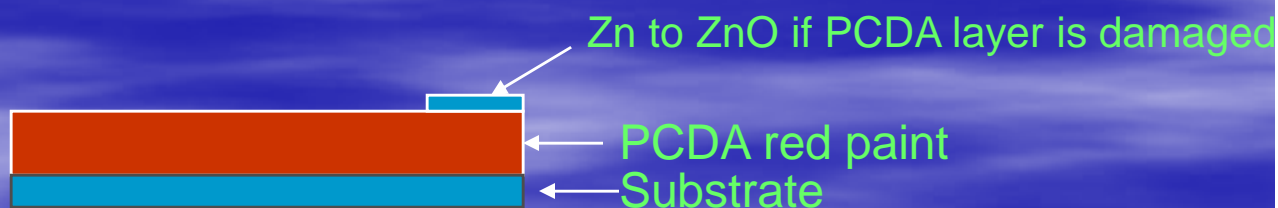
45% increase in yield strength relative to iron



Multilayer Smart Polydiacetylene Paint Coating



- If PCDA red layer is damaged, oxygen from the corroding substrate will react with Zn strip to form ZnO
- In presence of ZnO PCDA will undergo red to blue conversion – Raman data next slide



Monitoring blue and red PCDA phases in presence or absence of ZnO, ZrO₂ and TiO₂ by Raman scattering

Also note: Red phase is highly fluorescent



Summary

- Three types of nanotechnology-based passive and smart barrier coatings for corrosion protection discussed
 - Plasma-deposited conducting carbon polymer PPN can be used to protect small device or engine components and has been demonstrated to protect PEM fuel cell current collecting bipolar metal plates
 - Carbon nanotube paints/inks can form smart protective coatings via p-n junction layers which can electrically sense coating damage due to corrosion
 - Semiconducting, thermochromic polydiacetylene paints undergo irreversible color changes which can become reversible in the presence of chemical reactions induced by corrosion